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Motional effects between on-center and off-center substitutional nitrogen in silicon

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We have found for the first time that the hyperfine splitting of the ESR of off-center substitutional nitrogen in silicon increases with increasing the temperature above ≈ 150 K. A model is proposed in which a hypothetical on-center substitutional N site exists in an adiabatic potential-energy minimum higher than that of the off-center substitutional N. Motional averaging and narrowing among these configurations of the N center occur between ESR hyperfine lines and account for the increase in the hyperfine splitting. The fractional *s* character and localization of the unpaired electron at the on-center N seem to be significantly increased compared to those at the off-center N.

Nitrogen can be introduced into off-center substitutional sites in silicon by N-ion implantation and subsequent pulsed-laser annealing.[1,2] The dynamics of pulsed-laser annealing have been studied by several time-resolved measurements.[3-5] It is thought that the great effectiveness of pulsed-laser annealing for introducing the off-center substitutional N is caused by both the extremely fast recrystallization and rapid cooling.[3] Brower[1] revealed through ESR measurements that off-center substitutional N (labeled SL5) is trigonally distorted with C_{3v} symmetry about the ⟨111⟩ axis at temperatures below 100 K and has a deep level, similar to the N impurity in a type-1*b* diamond.[6] The distortion of substitutional N in Si is attributed to a pseudo-Jahn-Teller effect by recent theoretical calculations.[7]

In the present Rapid Communication, we report the strong temperature dependence observed for a ^{14}N ESR hyperfine (hf) spectrum and the possibility of an on-center substitutional N state. The temperature dependence can be explained in terms of motional effects of the unpaired electron among the four equivalent off-center N distorted along the ⟨111⟩ axis and hypothetical on-center N with T_d symmetry.

N ions (N_2^+) were implanted in Czochralski-grown B-doped (100) Si with the resistivity of 30–50 Ω cm and (111) Si with the resistivity of ≈ 120 Ω cm at an acceleration energy of 70 keV and a dose of $2\times10^{14}/\text{cm}^2$. The implanted samples were annealed with a *Q*-switched ruby laser at energy densities from 1.2 to 1.5 J/cm^2. The ESR measurements were made at temperatures ranging from 77 to 550 K with an *X*-band spectrometer. Off-center substitutional N is known to be annealed out at temperatures higher than 575 K for the Si samples implanted with a dose of $2\times10^{14}/\text{cm}^2$.[8]

We observe for the first time that the hf splitting of the ESR spectrum for off-center substitutional N (^{14}N: nuclear spin $I=1$, natural abundance 99.63%) increases without any change in the *g* value with increasing temperature. Typical ESR spectra observed at various temperatures for $H\parallel\langle100\rangle$ are shown in Fig. 1. The hf splitting ΔH_{hfs} is plotted as a function of temperature in Fig. 2. ΔH_{hfs} begins to increase at a temperature of 150 K. The ^{14}N hf spectra observed for $H\parallel\langle110\rangle$ and ⟨111⟩ exhibited the motional broadening in the linewidth at temperatures between 100 and 150 K; above 150 K, motional averaging and narrowing were observed,[9] as reported in Ref. 1. These motional effects come from the rapid reorientation of the ⟨111⟩ distortion in off-center N.[1] Therefore, we surmise that the increase in ΔH_{hfs} is related to motional effects since ΔH_{hfs} begins to increase at the onset of the motional narrowing. For comparison we measured also the temperature dependence of the ESR spectrum of the Si-SL6 center[1,8] which has a larger ⟨111⟩ distortion. The Si-SL6 center exhibits no changes in ΔH_{hfs}, as shown in Fig. 2, and no motional effects. These indicate that the change in ΔH_{hfs} is probably not due to a simple thermal expansion or gradual reduction in the ⟨111⟩ distortion, but is strongly related to motional averaging and narrowing of

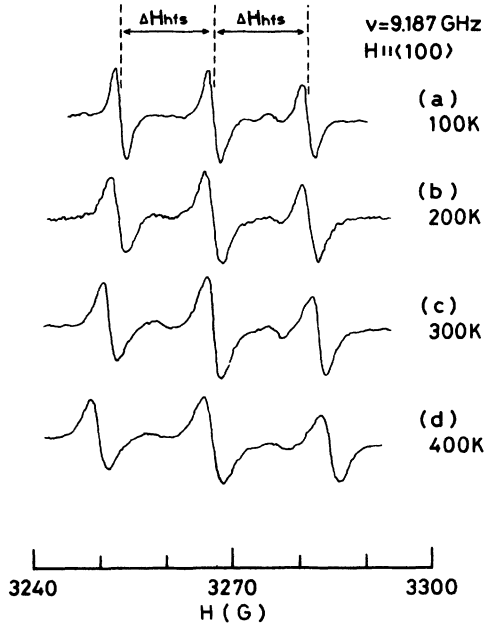

FIG. 1. Typical ESR spectra (a)–(d) of the substitutional ^{14}N in Si measured at various temperatures.

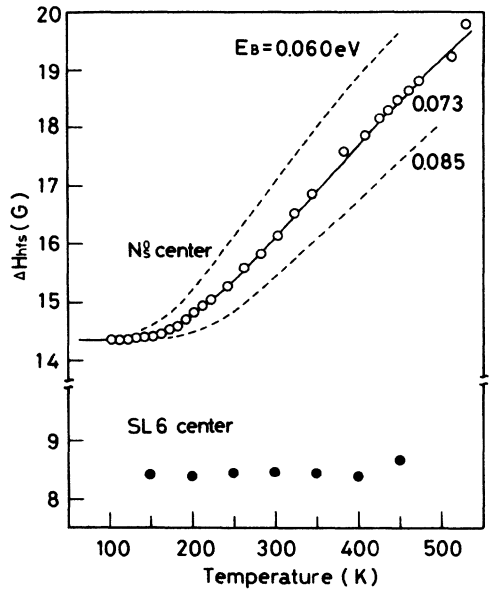

FIG. 2. Hyperfine splitting $\Delta H_{\rm hfs}$ of the ESR spectra of the substitutional N (N_s^0) and SL6 center as functions of temperature. The solid curve corresponds to the best fitting values of $E_B = 0.073$ eV and $\Delta H_{\rm hfs}\langle B\rangle = 134$ G, while dotted curves corresponding to other ones (0.060 eV and 134 G, and 0.085 eV and 134 G) for E_B are also shown for comparison.

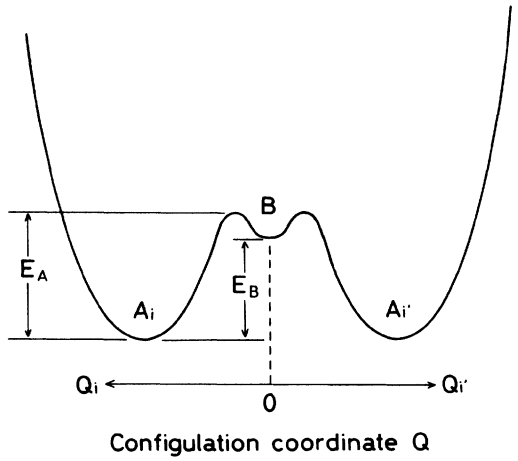

FIG. 3. Configuration coordinate potential-energy curve for the substitutional N in Si. At the potential minimum B at $Q_i = 0$, N occupies the substitutional lattice site, i.e., the on-center site, and at the potential minima A_i and $A_{i'}$ ($i,i' = 1, 2, 3$, or 4) N occupies the off-center site. For example, the configuration coordinate Q_i and $Q_{i'}$ correspond to the nitrogen displacement in the directions $[\bar{1}\,\bar{1}\,1]$, $[\bar{1}\,1\,\bar{1}]$, $[1\,\bar{1}\,\bar{1}]$, or $[1\,1\,1]$.

the ESR spectrum which is caused by the rapid reorientation increasing with raising the temperature.

In order to explain the change in $\Delta H_{\rm hfs}$, we propose a model in which substitutional N has two types of minima in the adiabatic potential, i.e., a shallow on-center well and a deeper off-center well (in the $\langle 111\rangle$ direction), and that N goes through the lattice site in its reorientation from one $\langle 111\rangle$ distortion to another. The on-center minimum was predicted by theoretical calculations by Deleo, Fowler, and Watkins[7] and Hjalmarson and Jennison.[10] These states are schematically shown in Fig. 3, using a configuration coordinate potential-energy curve. At temperatures higher than the onset (150 K) of motional averaging and narrowing, the unpaired electron moves around among states of the on-center minimum and the four equivalent off-center minima A_i ($i = 1$–4). We interpret our results in terms of the motional averaging and narrowing[11,12] occurring between both the hf line for substitutional N in the off-center states A_i and that for N in the on-center B state which have the same g value and different hf constants. In thermal equilibrium four A_i states occur with equal population probability p_A ($\approx \frac{1}{4}$) and the population probability p_B at the on-center minimum B becomes $\frac{1}{4}\exp(-E_B/kT)$ if $E_B > kT$. Here E_B is the energy difference between the on-center minimum and off-center minima, as shown in Fig. 3. $\Delta H_{\rm hfs}(T)$ is represented by

$$\Delta H_{\rm hfs}(T) = \Delta H_{\rm hfs}\langle A\rangle + \tfrac{1}{4}\exp(-E_B/kT)(\Delta H_{\rm hfs}\langle B\rangle - \Delta H_{\rm hfs}\langle A\rangle)\,, \tag{1}$$

where $\Delta H_{\rm hfs}\langle B\rangle$ and $\Delta H_{\rm hfs}\langle A\rangle$ are hf splittings of on-center N and off-center N, respectively.

As a result of fitting Eq. (1) to the experimental results, we obtain $E_B = 0.073$ eV and $\Delta H_{\rm hfs}\langle B\rangle = 134$ G, as shown in Fig. 2. The value of the energy difference E_B is compared to the barrier height $E_A = 0.107$ eV (Fig. 3) for the reorientation among four equivalent off-center sites which was obtained by Brower.[1] Furthermore, this result indicates that the on-center N has a deep level of ≈ 257 meV ($= 330 - 73$), since the off-center N has a deep level of ≈ 330 meV.[8,9] The wave functions of the unpaired electron for the on-center and off-center substitutional N are represented in terms of a one-electron antibonding molecular orbital,

$$\psi\{i\} = \sum_j \eta_j\{i\}\phi_j\{i\}\,, \tag{2}$$

where i is either A (off center) or B (on center) and $\eta_j\{i\}^2 (\sum_j \eta_j\{i\}^2 = 1)$ represents the degree of localization of the atomic orbital $\phi_j\{i\}$ at the jth atomic site. The index j ranges over N and the surrounding Si atoms. Here,

$$\phi_j\{i\} = \alpha_j\{i\}\,|s\rangle + \beta_j\{i\}\,|p\rangle\,, \tag{3}$$

where $\alpha_j\{i\}$ and $\beta_j\{i\}$ ($\alpha_j\{i\}^2 + \beta_j\{i\}^2 = 1$) are the fractions of the s and p character at the jth atomic site, and $|s\rangle$ and $|p\rangle$ are $|2s\rangle$ and $|2p\rangle$ for the N atom and $|3s\rangle$ and $|3p\rangle$ for the Si atom, respectively. From the value obtained for $\Delta H_{\rm hfs}\langle B\rangle$, we estimate $\alpha_N\{B\}^2\eta_N\{B\}^2$ for the on-center substitutional N to be 0.241, using a Fermi-contact hf constant A_F of 557 G (Ref. 1) for the valence electron of a neutral N atom. The value is much larger than $\alpha_N\{A\}^2\eta_N\{A\}^2$ of 0.0257 (Ref. 1) for off-center N. This indicates that the s character as well as the degree of

localization at the on-center N atom are enhanced compared with the off-center N. This result is consistent with an idea that the unpaired electron for the on-center N with T_d symmetry occupies an A_1 singlet band-gap level.[7,13]

If one of the four nearest Si sites surrounding N contains a ^{29}Si nucleus (nuclear spin $I=\frac{1}{2}$, natural abundance 4.7%), then there is a hf interaction between the unpaired electron and the ^{29}Si nucleus. A study of the motional effects on the ^{29}Si hf satellites is also informative for testing our model. This is shown in Fig. 4 for $H\|\langle 100\rangle$. At temperatures lower than 130 K the ^{29}Si hf satellites are clearly observed as in Figs. 4(a) and 4(b), while between 150 and 200 K the motional broadening occurs and so the intensity becomes very weak, as in Figs. 4(c) and 4(d). At temperatures above 200 K a motional averaged line that exhibited $\langle 111\rangle$ symmetry[9] can be seen at a magnetic field of ≈ 3237 G for $H\|\langle 100\rangle$ [Figs. 4(d)–4(f)]. This is just the averaged position between a ^{14}N line ($I_z=+1$) and a ^{29}Si line ($I_z=+\frac{1}{2}$), indicated by two solid arrows in Fig. 4(a); the unpaired electron sees the ^{29}Si hf field with a probability of $\frac{1}{4}$. In the motionally averaged state, the ^{29}Si hf satellites were also found to be about four times as intense relative to the central ^{14}N hf lines (see, e.g., Ref. 12).

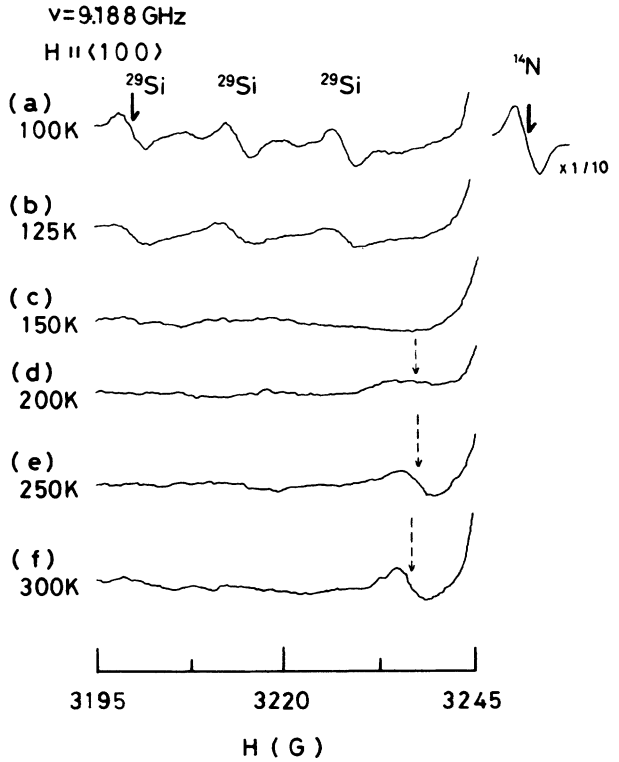

FIG. 4. Lower-field part of ^{29}Si hf lines in ESR spectrum of the substitutional N in Si for $H\|\langle 100\rangle$ and motional effects. Since the intensity of the ^{29}Si hf lines is very weak, we measured the ESR with a modulation-field of 5 G larger than the ESR linewidth. The dotted arrows in (d)–(f) show the motionally averaged position between the lowest one of ^{29}Si hf satellites and the lowest one of ^{14}N hf lines which are, respectively, indicated by the solid arrows in (a).

Above 200 K, we measured, moreover, the separation between the averaged ^{29}Si hf satellite and the low-field ^{14}N hf line. The separation was found to decrease slightly with raising the temperature. We estimated from this result that $a_{Si}\{B\}^2\eta_{Si}\{B\}^2$ was less than 0.02.[9] The values $a^2\eta^2$, a^2, and η^2 obtained for on-center N are given in Table I and are compared with those for off-center N.[1] This result suggests that the degree of localization, $\eta_{Si}\{B\}^2$, decreases down to $\lesssim 0.08$ if we make a guess of 25% s and 75% p for the atomic function of four equivalent Si atoms surrounding the on-center N atom. This result indicates that the unpaired electron density is $\lesssim 32\%$ ($=8\times 4$) localized on the nearest four Si sites. Thus the ^{29}Si hf structure indicates that even the on-center N still gives strong nearest ^{29}Si neighbor interactions as observed for the deep group-VI donors,[14] in contrast with the shallow group-V donors (P, As, and Sb) whose wave functions have nodes at the nearest neighbors. This also suggests that on-center N has a deep level rather than a shallow one.

Finally, we discuss the ratio of the s and p character and the degree of localization for the hypothetical on-center N in Si. According to a simple argument presented by Bachelet, Baraff, and Schlüter,[13] the state of the unpaired electron for on-center N is an antibonding A_1 type consisting of the dangling-bond–like singlet a_1 state of the Si lattice vacancy and $2s$ state of the N atom. Since the $2s$ level of the N atom is further from the A_1 level than the a_1 energy, i.e., the hybridization is asymmetric, $\eta_N\{B\}^2$ would be smaller than 0.5. If we take $\eta_N\{B\}^2$ to be 0.5 at most, then $\alpha_N\{B\}^2$ becomes 0.48, whereas if we take $\alpha_N\{B\}^2$ to be 1.0 (pure s-like) as in Refs. 7 and 13, $\eta_N\{B\}^2$ is estimated to be 0.24. These values estimated for the on-center N are much larger than those for the off-center N, as summarized in Table I. The $82(=50+4\times 8)\%$–$56(=24+4\times 4\times 8)\%$ unpaired electron density for the wave function $\psi\{B\}$ is localized on on-center N and the surrounding four Si sites, while the remaining 18%–44% of $\psi\{B\}$ is presumably spread over more distant Si neighbors. This value for the degree of localization of $\psi\{B\}$ is comparable to that calculated for on-center N in diamond[13] and silicon.[7] On the other hand, the remaining 18% of the wave function $\psi\{A\}$ is spread over the more distant Si neighbors.[1] Thus, this localization and s-like character are not inconsistent with our configuration coordinate model in Fig. 3.

TABLE I. s charactor and localization degree of the unpaired electron of substitutional N in Si. The second column contains the values obtained by Brower (Ref. 1).

	On-center N $\{B\}$	Off-center N $\{A_i\}$ $(i=1-4)$
$a_N^2\eta_N^2$	0.241	0.0257
a_N^2	1.0–0.48	0.28
η_N^2	0.24–0.5	0.09
$a_{Si}^2\eta_{Si}^2$	$\lesssim 0.02$	0.0876
a_{Si}^2	≈ 0.25	0.12
η_{Si}^2	$\lesssim 0.08$	0.73

In conclusion, we have found for the first time that the hyperfine splitting of a ^{14}N ESR sprectrum increases with increasing temperature above ≈ 150 K. From this result, we have deduced that a shallow potential well at the T_d substitutional site does exist, but has a configurational energy higher than that of the $\langle 111 \rangle$ distorted configuration by approximately 0.073 eV. Our results demonstrate that ESR measurements at relatively high temperatures can also be informative with regard to excited defect configurations which may be important in understanding the more complete dynamics of point defects in semiconductors.

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